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Interactive comment on “Production of N_2O_5 and $ClNO_2$ in summer in urban Beijing, China” *by* Wei Zhou et al.

Anonymous Referee #2

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The authors report four nights of N2O5 and ClNO2 observations in summer at an urban site of Beijing, China. The data were analyzed to show the concentration levels and N2O5 reactivity, and the N2O5 uptake coefficient and ClNO2 product yield were estimated from the field data. This manuscript provides a new piece of measurement data as well as some insights into the nocturnal N2O5 chemistry in the polluted atmosphere of North China. However, the current paper lacks some important details about the measurement and calculation methods, and some interpretation of the measurement results needs to be refined. Overall, this manuscript can be considered for publication after the following specific comments being addressed.

Major Comments:

Further details are required to clarify the quality assurance and quality control of the

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N_2O_5 and $ClNO_2$ measurements.

-The two CIMS systems were not in-situ calibrated during the measurement campaign. The UoM-CIMS was calibrated by the synthesized N_2O_5 and $ClNO_2$ after the campaign, and the IAP-CIMS was not calibrated and only inter-compared with the BBCEAS instrument. The sensitivity of the CIMS instruments may vary with the different operation conditions. Could the authors comment on the uncertainty of the post-campaign calibration on the present N_2O_5 and $ClNO_2$ observations.

-The inlet chemistry, including the potential loss of N_2O_5 and formation of $ClNO_2$ in the sampling inlet, is an important issue in the field measurements of N_2O_5 and $ClNO_2$, especially for the highly polluted areas such as the study site in the present study. Have the authors checked the inlet issue during the present measurements.

-The background of the CIMS instrument was determined by passing dry N_2 to the system in this study. The authors should provide a figure to show the background determination results, maybe in the supplementary materials. In addition, the authors may also need consider to check the instrument zero by adding excess NO to the ambient air, because the dry N_2 may be different from the real ambient conditions.

-It has been proposed that the ambient RH may affect the sensitivity of the CIMS to the target compounds. This may affect the analysis results of dependence of N_2O_5 reactivity on RH. The authors are suggested to further check the potential influence of ambient RH on their CIMS measurements.

-In view of the above issues, the authors should provide an overall estimation of their N_2O_5 and $ClNO_2$ measurements, at least including the detection limits and uncertainties.

On the calculation and analysis of the N_2O_5 reactivity:

-It seems that there were no VOC measurements in this study. It is not clear how the authors calculated $k(NO_3)$ and then N_2O_5 reactivity without the VOC data? If the

VOC measurements were available, the authors should provide the concentrations and chemical compositions of major VOC species.

-NO plays a very important role in the nocturnal N2O5 chemistry. Only a considerable level of NO (e.g., >1 ppbv) can significantly suppress the NO3 and then N2O5, as the reaction of NO3 with NO is very fast. This is why the concentrations of N2O5 and ClNO2 are usually low at surface sites in urban areas such as the study site in the present study. In comparison, the oxidation reactions of NO3 and VOCs are relatively slow, and NO3 can only oxidize a small group of specific VOCs, mainly biogenic VOCs and some oxygenated VOCs. The authors argued that the reactions of NO3 with VOCs are important for the N2O5 reactivity. It is better if the authors could separately evaluate the NO3 reactivity towards NO and VOCs.

-The authors assumed a steady-state for NO3 and N2O5 and estimated the lifetimes for these compounds (see Table 1). It is very strange that the lifetime of N2O5 was much shorter than that of NO3 radical. In general, the lifetime of NO3 radical is quite short, but N2O5 may have relatively longer lifetimes during the nighttime.

-Page 12, Lines 1-3: the Equation (6) was only valid if the observed nitrate increase was thoroughly contributed by the in-situ chemical production and the heterogeneous uptake of N2O5 contributed to 100% of the nighttime nitrate formation. The authors need consider the impacts of regional transport and other nitrate formation pathways on this calculation. As mentioned by the authors, previous studies suggested that the heterogeneous uptake of N2O5 only accounted for about 50-100% of nighttime nitrate formation. The authors at least should mention the assumption and limitation of this calculation method.

Page 13, Lines 20-22: this argument is not really true. The N2O5 production potential in P1 should be low because of its very high NOx levels. It is also a little bit strange that the concentrations of N2O5 and ClNO2 are moderately high given such high levels of NOx (>15 ppbv) in P1, but it is a very interesting result. What is the possible reason for this?

Page 13 Line 25 to Page 14 Line 2: this interpretation is not correct. The difference in the observed N2O5 and ClNO2 concentrations between P2 and P4 should be due to the difference in the NO levels, i.e., 0.5 versus 7.1 ppbv. Given your estimated short lifetimes of NO3 and N2O5, meteorological conditions and transport should not be the major factors here.

Page 15, Lines 6-11: on the low particulate chloride and its weak correlation with ClNO2, another possible reason is the size distribution of chloride aerosol. Only the chloride in PM1 was measured in this study, and it may largely underestimate for the total particulate chloride. Could the authors check the size distribution of chloride from the previous measurements available in urban Beijing and discuss its impacts on the observed results in this study.

Page 15, Lines 14-16 and 20-22: it was not clear how the N2O5 and NO3 reactivities were calculated without the VOC data. It would be better if the authors could also calculate the reactivity from heterogeneous N2O5 uptake, NO3+NO and NO3+VOCs, and compare them among each other.

Page 15, Lines 22-24: I guess that the higher N2O5 reactivity in P4 than P2 should be due to the higher NO level. The authors are encouraged to examine the detailed budget of N2O5 reactivity for both cases and find the exact reason for this.

Page 16, Lines 1-2: it is interesting that the N2O5 reactivity presents a non-linear dependence on aerosol surface area and RH. What are the possible reasons for this?

Page 16, Lines 6-14: it is interesting (and also strange) for the sharp decrease in the N2O5 reactivity with ambient RH from 40% to 50%. As mentioned above, the authors are suggested to examine the dependence of the CIMS sensitivity on the ambient RH.

Page 17, Lines 1-4: the authors are suggested to elaborate more about the air mass transport and its impacts on the observed N2O5 and ClNO2. What is the difference in the air mass origins among the four cases? Which air masses contained higher N_2O_5 and $ClNO_2$?

Page 18 Line 24 to Page 19 Line 4: as mentioned above, the reactions of VOCs and NO_3 are relatively slow, and NO_3 can only react with some specific VOC compounds. In comparison, the titration of NO_3 by NO is rather fast. Given the high NO levels observed in urban Beijing in this study, the NO_3 loss should be dominated by the NO titration.

Minor Comments:

Page 2, Line 6, "79.2 and 174.3 pptv": pay attention to the use of significant digits. What is the detection limit of the N_2O_5 and $ClNO_2$ measurements in the present study? Could it be up to 0.1 pptv? Please check and revise the usage of significant digits throughout the manuscript.

Page 2, Lines 6-8: does the N_2O_5 reactivity here include its indirect loss by NO_3? If so, the high N_2O_5 reactivity may not suggest the large nocturnal nitrate formation potential. Besides the heterogeneous reactions of N_2O_5, the nitrate formation also depends on the NO_3 reactivity and $ClNO_2$ product yield. After all, the authors also pointed out that the N_2O_5 loss was mainly attributed to the indirect loss by NO_3 (Page 2 and Lines 11-13).

Page 3, Line 2 "an efficient sink for the nocturnal removal of nitrogen oxides": "sink" is redundant with "removal", please rephrase this sentence.

Page 3, Lines 2-4: I suggest to separate this long sentence into two short ones, with one defining N_2O_5 and the other describing its thermal equilibrium with NO_3.

Page 3, Lines 4-5: I recall that the reactions of NO_3 with VOCs are not very fast. The N_2O_5 and NO_3 removal is mainly attributed to the rapid titration of NO_3 by NO in the high NO_x environments.

Page 3, Line 9: it should be particulate NO_3^-, other than HNO_3.

Page 3, Line 11: delete “N2O5” as only ClNO2 can be subject to photolysis to release NO3 and chlorine atom.

Page 3, Line 16: ClNO2 product yield. . .

Page 4, Lines 5-7: on the inconsistency between field-derived N2O5 uptake coefficient and the lab-derived parameterizations, the authors should acknowledge the work of Brown et al. 2006.

Brown, S. S., et al.: Variability in nocturnal nitrogen oxide processing and its role in regional air quality, Science, 311, 67-7-, 2006.

Page 4, Lines 10-12: regarding this indirect measurement approach, what technique was used for the measurement of NO3 radical?

Page 4, Lines 13-15 and 17-19: please also refer to the following measurement works of N2O5 and ClNO2 by CIMS in China.

Tham Y. J., et al.: Presence of high nitryl chloride in Asian coastal environment and its impact on atmospheric photochemistry, Chinese Sci. Bull., 59, 356-359, 2014.

Wang T., et al.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res., 121, 2457-2475, 2016.

Tham Y. J., et al.: Significant concentrations of nitryl chloride sustained in the morning: investigations of the causes and impacts on ozone production in a polluted region of northern China, Atmos. Chem. Phys., 16, 14959-14977, 2016.

Page 4, Lines 8-19: the description of the commonly used measurement techniques for N2O5 and ClNO2 is incomplete here. The authors need also briefly introduce the Cavity Ring-Down Spectroscopy (CRDS) and the CIMS with an unheated inlet configuration (235 m/z).

Page 4, Line 22: change “several” to “some”, as there have been about a dozen mea-

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surement studies of N_2O_5 and $ClNO_2$ in China.

Page 5, 1-2: besides these measurement efforts, recently, some modeling studies have also evaluated the impacts of N_2O_5 and $ClNO_2$ chemistry on the ozone formation and regional air quality in China. The authors should consider to include these efforts to enrich the current understanding of the nocturnal nitrogen chemistry and its impacts.

Xue L. K., et al.: Development of a chlorine chemistry module for the Master Chemical Mechanism. Geosci. Model Develop. 8. 3151-3162, 2015.

Wang T., et al.: Observations of nitryl chloride and modeling its source and effect on ozone in the planetary boundary layer of southern China, J. Geophys. Res., 121, 2457-2475, 2016.

Li Q. Y., et al.: Impacts of heterogeneous uptake of dinitrogen pentoxide and chlorine activation on ozone and reactive nitrogen partitioning: improvement and application of the WRF-Chem model in southern China, Atmos. Chem. Phys., 16, 14875-14890, 2016.

Page 5, Line 9: delete “However”

Page 5, Lines 15-17: a recent modeling study has evaluated the impacts of heterogeneous $ClNO_2$ formation on the next-day ozone formation in Beijing.

Xue L. K., et al.: Ground-level ozone in four Chinese cities: precursors, regional transport and heterogeneous processes, Atmos. Chem. Phys., 14, 13175- 13188, 2014.

Page 6, Line 7: provide standard deviations for the average values of temperature and RH.

Page 8, Lines 3-5: how did you estimate this uncertainty?

Page 9, Line 20: was the slope of 1.42 derived from the least square regression method? Such slope indicates an average difference of 42% between the two CIMS instruments. Which one gave higher concentrations?

Page 10, Lines19-20: k(N2O5) is commonly used to refer to the heterogeneous reaction rate of N2O5, other than the uptake rate coefficient.

Page 13, Line 2: at Mt. Tai. . .

Page 13, Lines 6-14: please provide the observed concentrations levels of NO and NO2, and also discuss the impact of NOx on the observed variations of N2O5 and ClNO2. As mentioned above, NOx play a very important role in the variability of N2O5 and ClNO2.

Page 13, Line 10: residual boundary layer. . .

Page 13, Lines 15-18: as introduced in the introduction, there have been many studies of N2O5 and ClNO2 in both North China Plain (e.g., Mt. Tai, Beijing, Wangdu, Jinan) and Hong Kong. It would be better if the authors could compare the observed results in this study to these previous results. Is there any difference between the NCP region and Hong Kong in southern China?

Page 13, Lines 20-21: provide the units for 2.8 and 3.6.

Page 14, Line 13: rephrase this sentence. Is there any relationship between the N2O5 formation and the decrease in p(NO3)? p(NO3) is only dependent on the abundances of both O3 and NO2. If anything, the decrease in p(NO3) should weaken the N2O5 formation.

Page 15, Lines 3-4: the reference of Riedel et al. 2012 is not relevant here. It was conducted in US, not in Beijing.

Page 15, Line 6: high emissions from human activities. . .

Page 15, Lines 13-14: it is not clear why only the two-hour data after sunset was used here. Please clarify.

Page 15, Lines 18-19: provide the numbers for the N2O5 loss in southern China and USA for easy comparison.

Table 1: provide the standard deviations and units for the aerosol species.

Figure 1: provide the time series of the aerosol surface area concentrations.

Figure 2: provide the units for N_2O_5 and $ClNO_2$.

Figure 4: provide the slopes for the regression analysis.

Figure 6: plot the wind sectors to show if the metrological conditions were stable.

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